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T. Spalvins
Lewis Research Center
Cleveland, Ohio



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VACUUM SPUTTERED AND ION-PLATED COATINGS FOR WEAR AND CORROSION PROTECTION

T. Spalvins
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

The plasma or ion-assisted coating techniques such as sputtering and ion-plating are discussed in view of wear and corrosion protection. The basic processes and the unique features of the technique are discussed in regard to the synthesis and development of high reliability wear and corrosion-resistant films. The ions of the plasma which transfer energy, momentum, and charge to the substrate and the growing films can be beneficially used. As a result, coating adherence and coherence is improved. Favorable morphological growth can be developed such as high density and porosity-free films and residual stresses can be reduced.

INTRODUCTION

The coatings deposited by the vacuum deposition techniques can provide effective protection for mechanical components or structures from wear, erosion, corrosion, and oxidation. The vacuum deposition techniques can be considered as atomistic processes since the coatings are grown atom by atom at low pressures and are generally free of imperfections such as porosity or inclusions of detrimental impurities. A detailed structural characterization is of prime importance; it is this information from the atomic level right up to the macroscopic level which is needed to determine bonding across the interface region, nucleation, and growth characteristics.

The effectiveness of a wear or corrosion-resistant coating depends primarily on the coating technique selected. The tribological and corrosion characteristics are affected primarily by coating adherence, coherence and morphology. The degree of adherence is directly related to the surface pretreatment and type of interface formed, but the morphology (nucleation and growth) is directly affected by surface finish, cleanliness, and the evaporation flux. These aforementioned factors determine the coating wear, and durability, and the type of corrosion mechanism.

In the last two decades the plasma or ion-assisted vacuum deposition techniques (sputtering, ion plating) have emerged to offer a great potential in supplementing the well known physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques. Plasma, often referred to as "the fourth state of matter," is an ionized gas, and a convenient source of energetic electrons, ions, and activated energetic evaporants which can be used in a variety of surface treatment processes.

In this review particular attention is directed to the sputtering and ion plating techniques which offer unlimited potentials to synthesize and deposit coatings for wear and corrosion control. These techniques are restricted to processes where particle condensation on the substrate is initiated under the direct action of either ion flows or energetic neutrals produced by charge exchange. The recent interest and activity in these

techniques originates from the fact that any material in any desired chemical composition can be synthesized and deposited with a preferred morphological structure. The increased energizing of the deposition process generally leads to improved film adherence, favorable morphological growth, higher density, and reduced residual stresses in the film. In addition, these coatings are generally thin enough ($<2\text{ }\mu\text{m}$) so that for all practical purposes the finished dimensions are unchanged by the coating process, and the surfaces coated are not subjected to high temperatures. The outstanding protective characteristics of these thin coatings can not be obtained by even much thicker coatings prepared by other coating techniques.

Over the past several years rapid advances have been made in the sputtering and ion-plating equipment design, with the objective to increase the ionization efficiency of the evaporant flux. The enhanced ionization affects the nucleation and growth sequence which, in turn, favorably affects the crystallographic structure and the morphological growth. The columnar structure which is characteristic of most coating techniques causes mechanical weakness due to the high porosity and internal stresses and has poor corrosion protection. The enhanced ionization has the tendency to form a more equiaxial structure with a smaller grain size and higher density, contributing to an increased cohesive strength and eliminating porosity.

With the enhanced ionization, activation energy is also increased which promotes chemical reactions when reactive gases such as N_2 or C_2H_2 , are introduced to form the respective wear-resistant nitrides and carbides. In the reactive mode of sputtering and ion-plating, concurrent synthesis and deposition can be performed with a wide compositional range to generate the optimum properties for wear resistance.

The objective of this paper is to describe the unique characteristics and the potentials of the sputtering and ion-plating processes and the resultant coating characteristics which can be developed to favorably affect the tribological and corrosion behavior.

SPUTTERING FEATURES AND ITS POTENTIALS

The sputtering technology offers a great versatility and flexibility in coating preparation, since the sputtered coatings can be tailored in any preferred chemical composition, and the coating morphologies can be modified. The sputtering process is not regulated by classical thermodynamics and Gibb's phase rule relationships. As a result, one is not confined within the framework of the rigid phase relationships. Any combination of metal and non-metal elements can be sputter-deposited in any composition, without concern for their phase relationships.

From an industrial point of view, the following unique sputtering features are an integral part of the process: versatility in material deposition, momentum transfer (impact evaporation), sputter-etching, precise controls (stoichiometry, uniformity, thickness), high flexibility in selecting sputtering modes and configurations, and elimination of ecological problems. These features have been widely described in the literature (refs. 1-4).

Two basic types of sputtering can be distinguished, depending on whether the glow discharge plasma is generated by direct current (dc) or radio frequency (rf) fields. A wide variety of sputtering modes and configurations are used. However, all of these arise essentially from (1) the way in which plasma is generated (dc, rf, auxiliary electrodes), (2) the target and substrate positioning and their geometrical configurations, (3) the number

of sputtering targets in the system, (4) the type of gases used (inert or reactive), and (5) the use of magnetic fields—magnetron sputtering. A typical radio frequency diode sputtering apparatus with dc bias is shown schematically and photographically in Figure 1. In rf sputtering the target is energized by the application of rf (13.56 MHz) power. The rf current through the target injects power into the inert gas, thus generating the ion plasma by rf fields. Further, the rf field generated in the glow discharge prevents charge accumulation and, as a result, insulating materials and dielectrics can be sputtered.

When the refractory compounds such as carbides and nitrides are sputter-deposited, the appropriate reactive gas such as N_2 or C_2H_2 is introduced into the system. The flow rate is carefully controlled to maintain the corresponding stoichiometry or synthesize the desirable chemical changes in the coating. Further, TiN films also display different attractive gold-like colors when Ti is sputtered in a N_2 -Ar gas mixture as the partial pressure of N_2 is varied. The color is important for decorative applications and also protects the surface against wear and corrosion. The color can be also used as an indication of film characteristics such as hardness and resistance to wear and corrosion.

It has been reported (ref. 5) that the N_2 flow rate above a certain critical level results in a darkened film without exhibiting the pleasing gold-like appearance. These darkened films have lower hardness and less resistance to abrasion and corrosion.

A new class of complex coatings known as MCrAlY have been developed, where M can be Ni, Co, NiCo, Ta, and Hf. These coatings are extensively used to coat aircraft mechanical components such as blades and vanes of a gas turbine engine, where the high temperature hostile environment causes hot corrosion, high temperature oxidation, diffusion, and fatigue. A sputtered turbine blade is shown in Figure 2. It should be emphasized that sputtering is the proper technique to deposit these complex alloy coatings with high precision and reliability.

ION PLATING PROCESS AND ITS POTENTIALS

Ion-plating combines in principle the high throwing power of electroplating, high deposition rates of thermal evaporation, and high energy impingement of ions and energetic atoms of the sputtering process. The basic difference between sputtering and ion-plating is that in sputtering the coating material is generated by impact evaporation and transfer occurs by a momentum transfer process; whereas, in ion-plating generation is by thermal evaporation and transfer is by electric field acceleration. The ion-plating process is more energetic than sputtering, since a high substrate bias of several thousand volts accelerates the positively ionized evaporant atoms into the substrate. The basic ion-plating system consists of a dc-diode configuration, where the specimen is made the cathode of the high voltage dc circuit, with an evaporation source as anode (Fig. 3). The ion-plating technique and the process parameters are described in the literature (refs. 6 to 11).

The interest in ion-plating originates from its three unique features: 1) The high energy flux of ions and energetic neutrals contributes to the excellent adherence of the film to the substrate and the desirable microstructural growth of the film; 2) when used in the reactive mode this flux provides activation energy to synthesize stoichiometrically uniform compound films; and 3) the high throwing power provides for 3-dimensional coverage to

coat complex, intricate components such as internal and external surfaces without component rotation at high deposition rates (shown in Fig. 4.)

Under typical ion-plating conditions (voltage, 3-5kv; argon pressure, 20 mTorr; and cathode current density, 0.3 to 0.6 mA/cm²), the ionization is relatively low: less than 1 percent. It has been estimated that under these conditions the ions carry only 10 percent of the energy dissipated, while the energetic neutrals carry 90 percent (ref. 6). Thus the plating flux consists of a small number of ions and a large number of energetic neutrals. The ions and the neutrals may have a distribution of energies from thermal 0.2 eV up to the voltage applied to the discharge. Estimates indicate that the average energies of the ions and the neutrals are of the order of 100 eV (ref. 6).

The reactive mode of ion-plating shows distinct advantages in the deposition of the wear-resistant refractory compounds. It offers excellent adherence due to the formation of a graded interface. Also the nitrides and carbides such as TiN and TiC can be stoichiometrically synthesized and uniformly reproduced (refs. 12-14). It is important to understand that from a tribological or corrosion point of view, the excellent adherence is not the only controlling factor for optimum wear and corrosion resistance. The microstructure and morphological growth of the coating is of equal importance. Although conventional ion-plating does improve the grain structure, the structure still tends to be columnar. The objective is to increase the ionization efficiency which affects the nucleation and growth sequence, to producing fine equiaxed structures of high density at lower temperatures. Increased ionization has been achieved by providing additional ionization sources such as a thermionic emitter or positive electrode. These enhanced ionization techniques generally increase the ionization ratio by a factor of 10 and are used mainly for the deposition of hard wear-resistant coatings.

ION BOMBARDMENT EFFECTS ON COATING CHARACTERISTICS

During sputtering or ion-plating, ions transfer energy, momentum, and charge to the substrate and the growing films. Even without acceleration the ionized species greatly influence the critical parameters of the condensation and nucleation process for film formation. An interrelationship exists between the film formation characteristics, structure, chemical composition, and wear and corrosion-resistant properties which are strictly controlled by the deposition parameters and the substrate condition.

The basic objectives in the deposition of wear and corrosion-protective films are strong adherence and coherence, low internal stresses, and change from the columnar structure to a more dense, isotropic, equiaxed structure. For instance, the hard wear-resistant coatings of Cr, TiN, TiC, and CrC will also be corrosion-resistant if dense, adherent coatings are formed without pores reaching the base metal (since pitting is a localized breakdown of the film, which allows corrosion to begin on the bare metal).

The plasma-deposition techniques have no adverse environmental impacts on the coated components. Because of this distinct advantage, ion-plating is rapidly displacing the conventional electroplating techniques to plate corrosion-protective Al, Zn, and Cd films on high strength, low alloy steels. Usually steels harder than Rc40 are susceptible to hydrogen embrittlement during electroplating which, consequently, lowers the useful stress level of the component.

Adherence

Adherence and interface formation are of paramount importance since these characteristics determine the mode of wear or the type of corrosion. When a coating is deposited the coating/substrate interface represents a break in the normally uniform crystallinity and/or composition. This abrupt change or mismatch is reflected in the hardness, coefficient of thermal expansion, and thermal conductivity. This discontinuity may be reduced or eliminated by inducing a gradual transition from the interface to the outer surface of the coating. For instance, a hardness gradient can be produced (as shown in Fig. 5 for TiN) either by reactive sputtering or reactive ion-plating by varying the composition of the reactive gas. These techniques are extensively used in metalworking and forming operations to improve the working surfaces of cutting and forming tools with a carbide or nitride coating.

In ion plating, protective films of Cr, Ni, and Au can be deposited at a constant pressure due to the formation of a graded-fused interface. The graded interface, and consequently the strong adherence, is generally attributed to the sputter-etched surface and the high energy evaporant flux. The exact mechanism for the formation of such an interface is not fully understood, but the controlling factors are a sputter-etched surface, diffusion, implantation, atomic mixing, and nucleation and growth (shown in Fig. 6). These factors can act separately or in various combinations depending on the film/substrate compatibility. The graded interface formed is not only responsible for the excellent adherence but also affects the mechanical behavior, due to a structural alteration of the crystal lattice in the surface and subsurface regions. The surface-strengthening effects created can increase the yield, tensile, and fatigue strengths, as shown in Fig. 7.

Structure

The structure of deposited coatings can be improved by increasing the substrate temperature. For instance, the chemical vapor deposition (CVD) techniques are industrially used to deposit TiN and TiC coatings on cemented carbide cutting tools to improve their cutting performance. The drawback of the CVD technique is the high temperature required for optimizing the adherence and structural integrity. Temperature-sensitive materials (such as alloy tool steels used as cutters, and drills) can not be directly CVD coated with TiN or TiC since the processing temperature is usually above 900° C (above the tempering temperature of the steel). Under these conditions the substrate material is exposed to dimensional and phase changes and a reduction in hardness.

It is well recognized that films prepared by sputtering show a wide range of microstructures as the substrate temperature increases. This has led to the development of the structure zone model (SZM) shown in Figure 8 (ref. 15). The model consists of the formation of four zones which depend on the ratio of the surface temperature (T) to the melting point of the deposited material (T_m). The structural T/T_m dependence is affected by the surface diffusion processes and the bulk processes that characterize recovery and recrystallization (ref. 15). The coatings in zone 1 have tapered columnar crystals separated by open, voided longitudinal boundaries, rather than true grain boundaries. This structure is characteristic of electroplating and most coating techniques, and causes mechanical weakness and an easy diffusion path for corrosive gases. Coating in zone T (transi-

tion) region consists of densely packed fibrous grains. In zone 2 the structure has columnar grains separated by distinct, intercrystalline boundaries. Finally, in zone 3 bulk diffusion has predominant influence on the final structure of the coating and consists of equiaxed, dense, recrystallized grains.

Recovery and/or recrystallization reduces the internal stresses; this type of structure is preferred for the deposition of wear-resistant high-melting refractory compound coatings. However, the high T/T_m required for carbide and nitride deposition unfavorably affects the substrate materials such as tool steels. This high temperature limitation can be overcome by intensifying the glow discharge. For example, by increasing the specimen to substrate current density which has the same effect as raising T/T_m directly, a structure characteristic of the higher zone can be developed.

To maximize the specimen ion current, additional ionization sources such as positive electrodes or thermionic emitters are incorporated in the ion-plating system to provide a triode configuration. These additional electrodes are used to intensify the discharge. They also allow for the varying of discharge current independently from the bias voltage on the specimen. This high energy evaporation flux offers a means of obtaining dense, fine grained, equiaxial microstructures representative of a higher T/T_m . This approach had been primarily investigated and developed for the deposition of carbides and nitrides. Additional energy applied to the condensate increases the bombardment effects during the deposition which favorably influences the nucleation and growth characteristics.

It has been reported that high energy (>500 eV) ion bombardment can suppress the formation of a distinct columnar structure (ref. 9). The high rate of nucleation tends to form a uniform, fine-grained, high-packing density smooth film which contributes to an increased cohesive strength. This increased cohesive strength improves the film's integrity, thereby reducing the likelihood of a break-up of the coating during the wear process. For instance, during ion-plating the evaporant ions and energetic neutrals have a strong surface interaction, thereby limiting the surface mobility and, at the same time, increasing nucleation density. This leads to the formation of a fine, uniform, and continuous grain structure. A typical comparison of a vapor-deposited and ion-plated gold crystalline structure is shown in Figure 9. Continuous dense films are obtained at a lower nominal thickness using ion-plating.

Internal Stresses and Film Thickness

The hard wear-resistant refractory compound films are generally in a state of high stress. The total internal stress is composed of the thermal stress σ_t and intrinsic stress σ_i :

$$\sigma_{tot} = \sigma_t + \sigma_i$$

The thermal stress is due to the differences in the thermal expansion coefficient of the coating and the substrate material. This difference is very pronounced between the refractory compound coatings and the metallic substrate. Intrinsic stress is due to the accumulating effects of crystallographic defects or flaws formed in the coating during deposition.

Typical deposition conditions normally involve relatively low temperatures. At low T/T_m the intrinsic stresses dominate over thermal stresses, as shown in an idealized representation in Figure 10 (ref. 16). Thus the poor adhesion for the high melting point materials (carbides and nitrides)

can be attributed to the intrinsic stresses. In addition to the temperature effects (T/T_m) which affect the internal stress values, the degree of ion bombardment also strongly influences the internal stresses. With increasing ion flux, the stress changes from tensile to compressive in nature. Typically evaporated films retain high tensile stresses, while sputtered films may have low tensile or compressive stresses depending on the nature of energetic ion and neutral bombardment. Ion-plating, which has the highest energy flux, generates a graded-fused interface where the compressive stresses are distributed and appreciably reduced.

The film stresses also vary with film thickness. As a critical thickness is exceeded, poor adherence is caused by cracking or buckling. Whenever the shear stress exceeds the yield stress at the interface or within the film itself, separation will occur. A typical film delamination within a sputtered Cr_3C_2 film about $3.5\text{ }\mu\text{m}$ thick is shown in Figure 11. Film thickness is also critical for soft metallic (Au, Ag, Pb) lubricating films in order to achieve the lowest coefficient of friction. The variation of the friction coefficient with film thickness for ion plated Pb and Au films is shown in Figure 12. The optimum film thickness for Au and Pb films was $0.2\text{ }\mu\text{m}$.

Substrate Topography

In addition to the process parameters, the surface topography of both the substrate and resultant coating has a pronounced effect on the wear behavior. It is impossible to prepare surfaces that are atomically smooth over extended areas; macrodefects, however, can be eliminated. Microdefects such as dislocations and point and extended defects limit obtaining a smooth surface. Various unusual crystallographic defect growth structures are observed in the matrices of sputtered and ion-plated carbide, nitride, and silicide films. Typical SEM micrographs in Figure 13 show the surface views of sputtered MoSi_2 and Cr_3C_2 films with defect growth features. Substrate irregularities or imperfections are the preferential nucleation and growth sites of these defects. At these nucleation sites, accelerated growth occurs relative to the matrix growth, and as a consequence, the crystallographic defects extend above the matrix surface. These surface defect structures are stress-raisers which weaken the film structure by fracturing, and become and also are potential sources for damaging abrasive wear particles. These crystallographic defect structures have the greatest damaging effects on the hard wear-resistant coatings.

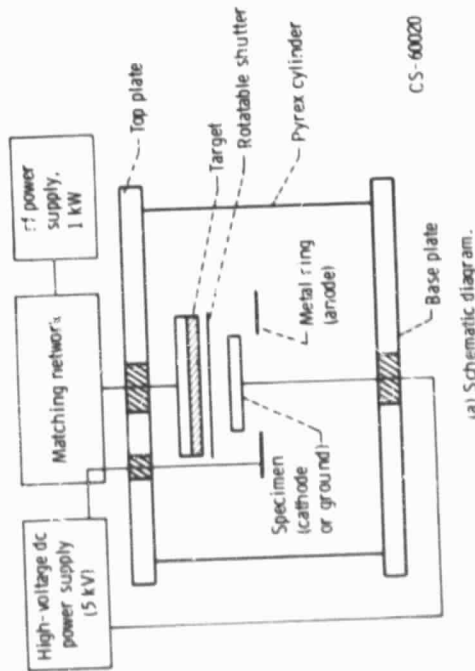
CONCLUSIONS

The plasma or ion-assisted vacuum deposition techniques such as sputtering and ion-plating have rapidly emerged to offer a great potential for depositing wear- and corrosion-resistant coatings. The basic processes and unique characteristics of sputtering and ion-plating should be understood in order to synthesize films resistant to wear and corrosion. These techniques offer a great flexibility in tailoring chemical composition and modifying the morphologies to suit specific applications. The energetics of the plasma can be used favorably to improve coating adhesion, and cohesion, develop favorable morphological growth, and higher film density, and reduce residual stresses. The disadvantage of these coatings lies mainly in their newness; that is, the best coating compositions and the optimum processing parameters have yet to be established.

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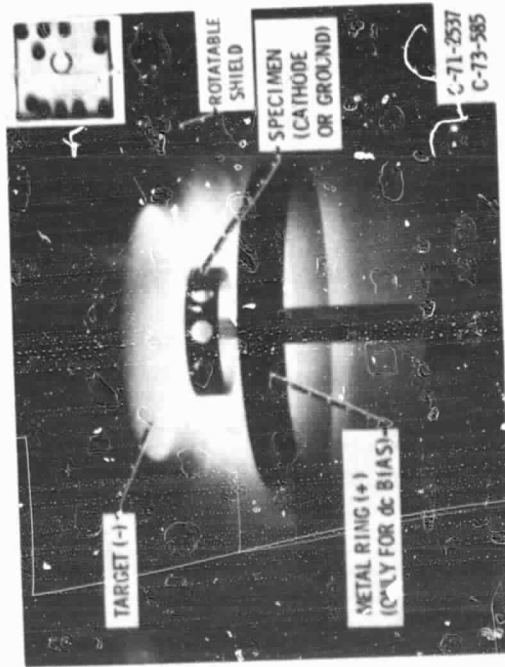
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(a) Schematic diagram.



(b) View of apparatus during sputter coating.

Figure 1. - Radiofrequency diode sputtering apparatus with direct-current bias.

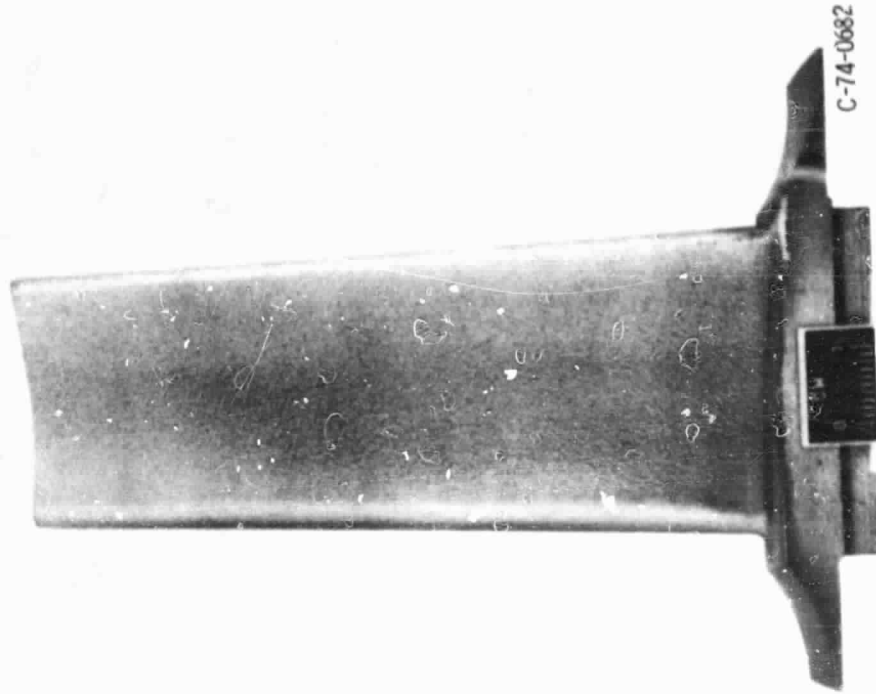
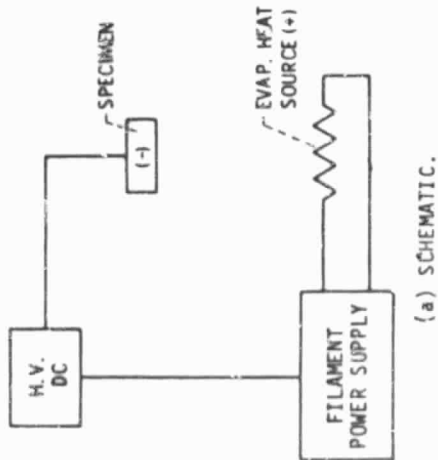
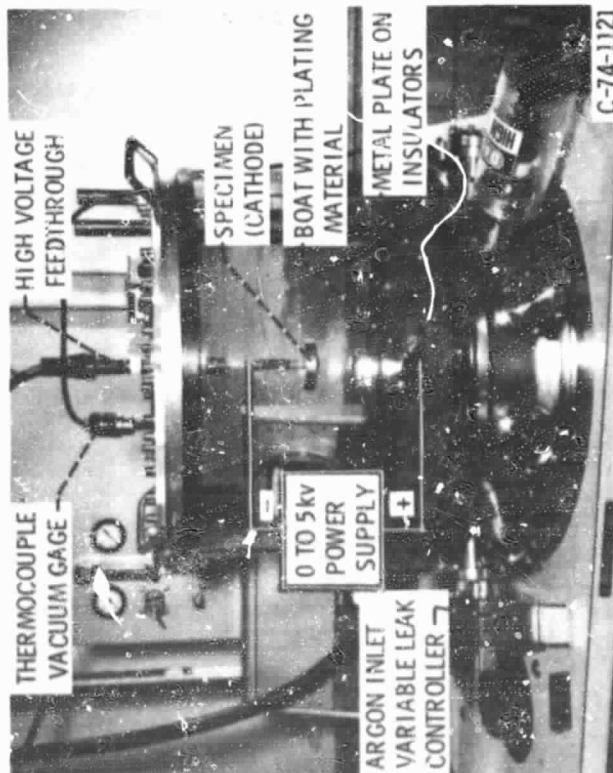


Figure 2. - Turbine blade sputter coated with MCrAlY.

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(a) SCHEMATIC.



(b) ION PLATING CHAMBER.
Figure 3. - Ion plating system.

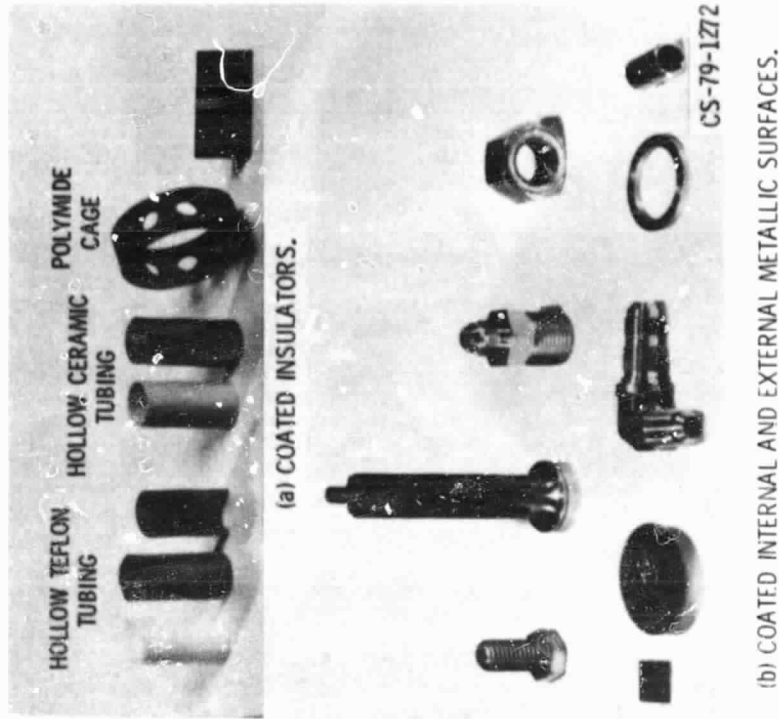


Figure 4. - Ion plated insulators and objects with metallic coating.

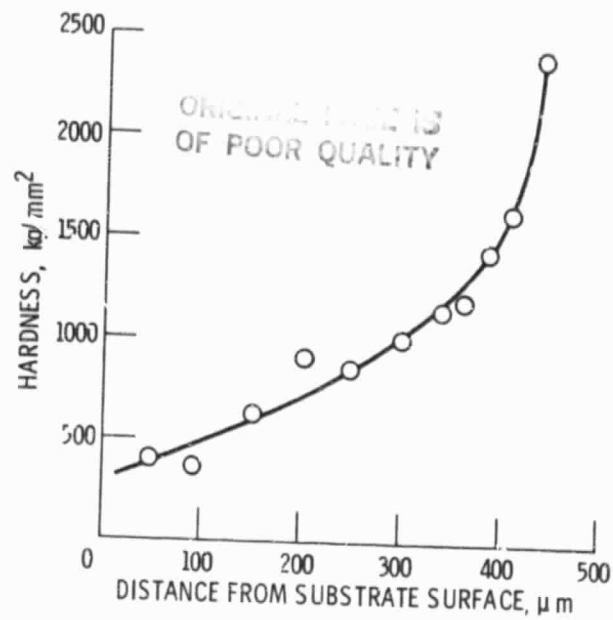


Figure 5. - Hardness gradient of TiN coating produced by reactive ion plating.

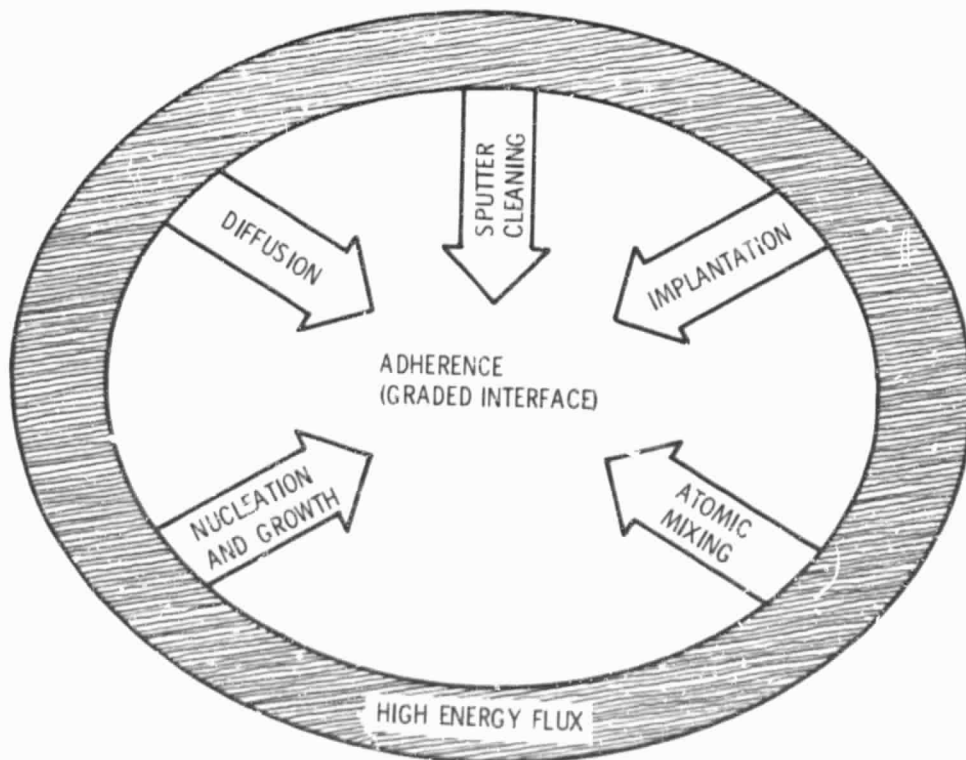


Figure 6. - Illustration of the factors which influence adherence and interface formation during ion plating.

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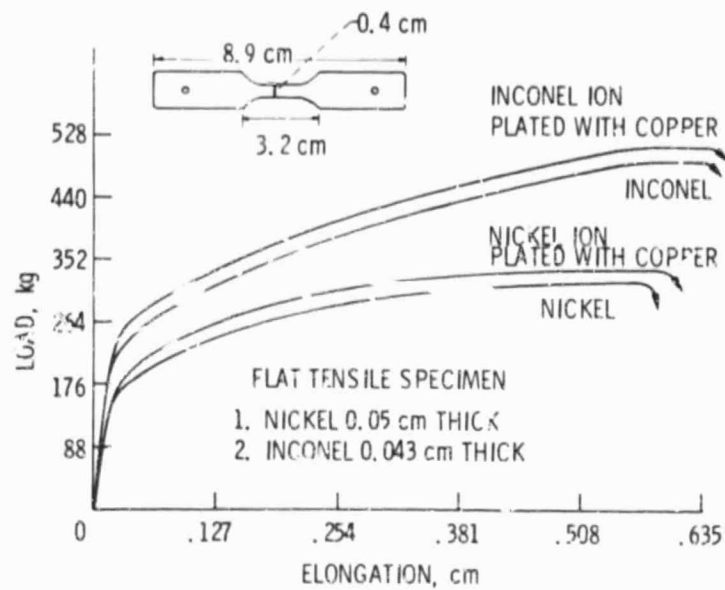


Figure 7 (a). - Load elongation curves during tensile tests.

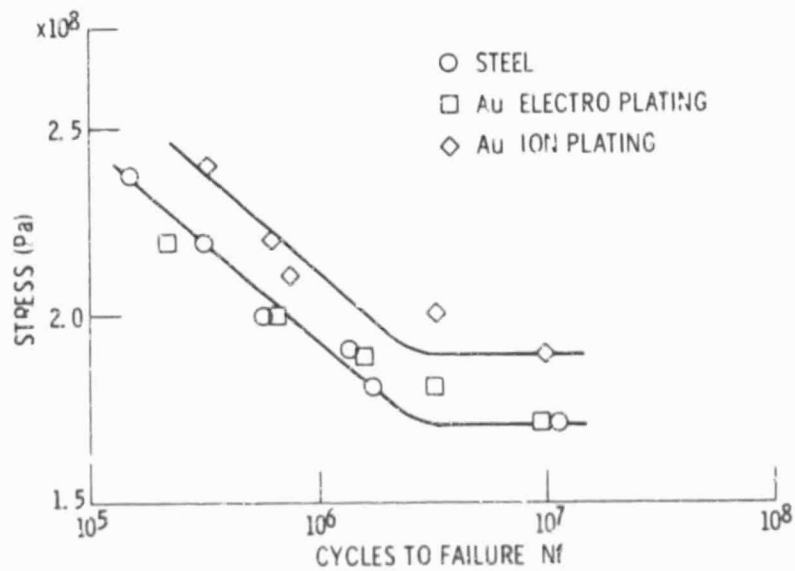


Figure 7 (b). - Effect of ion plating on the fatigue property of low carbon steel (ref. 13).

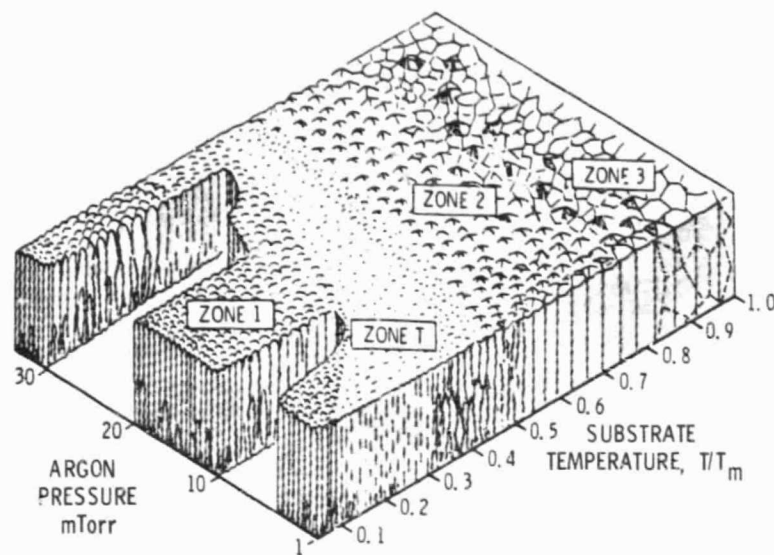
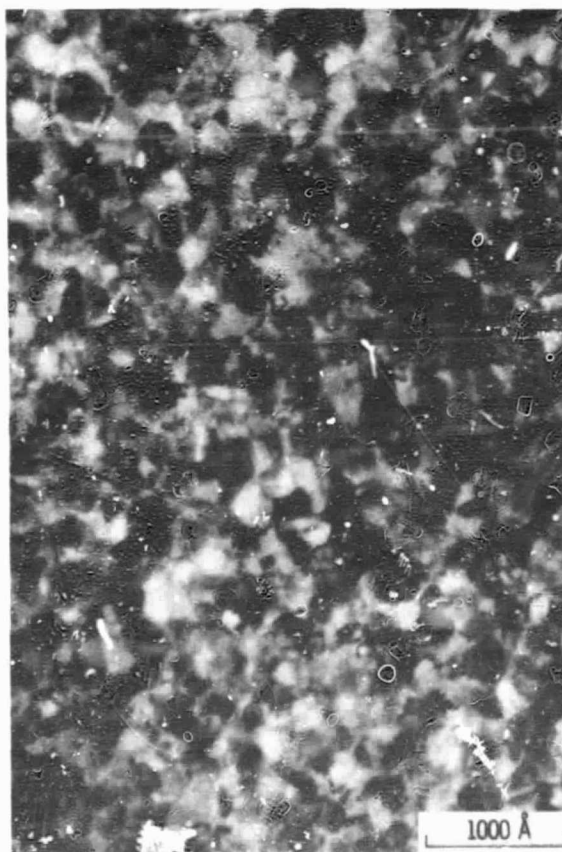


Figure 8. - Schematic representation of the influence of substrate temperature and argon working pressure on the structure of metal coatings deposited by sputtering using cylindrical magnetron sources. T is the substrate temperature and T_m is the melting point of the coating material in absolute degrees (ref. 15).



(a) ION PLATED GOLD.



(b) VAPOR DEPOSITED GOLD.

Figure 9. - TEM micrograph of the crystalline structure of gold film.

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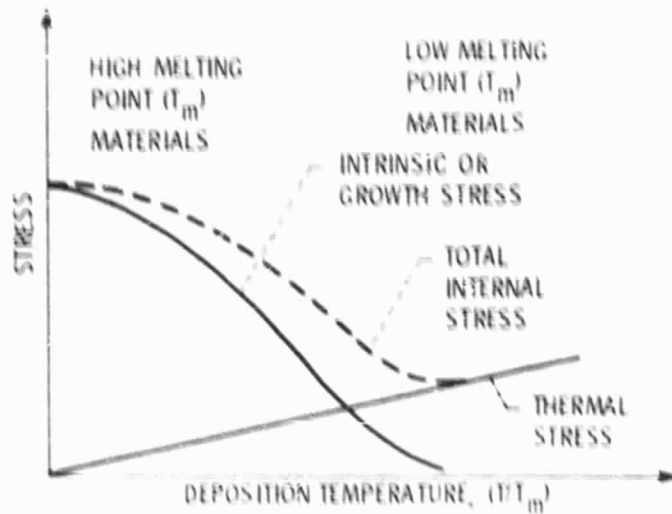


Figure 10. - Schematic representation of thermal and intrinsic stress contributions (ref. 16).

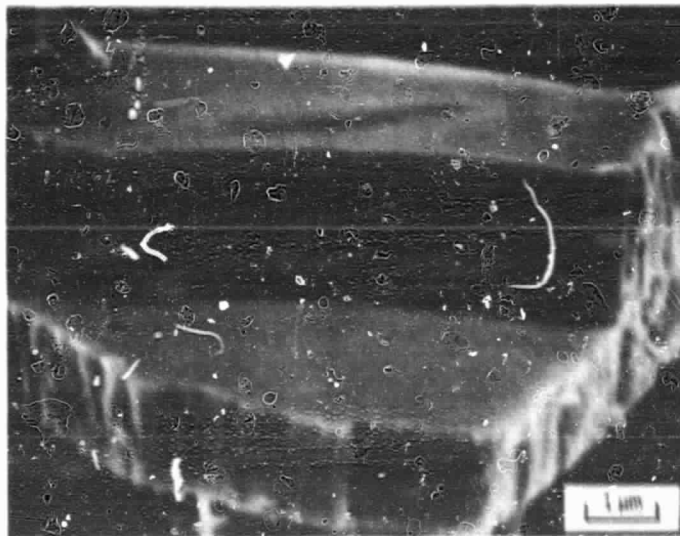


Figure 11. Separation within a 3.5 μm film of sputtered Cr_3C_2 .

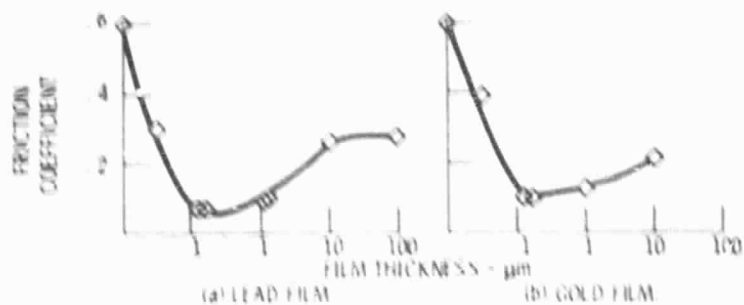
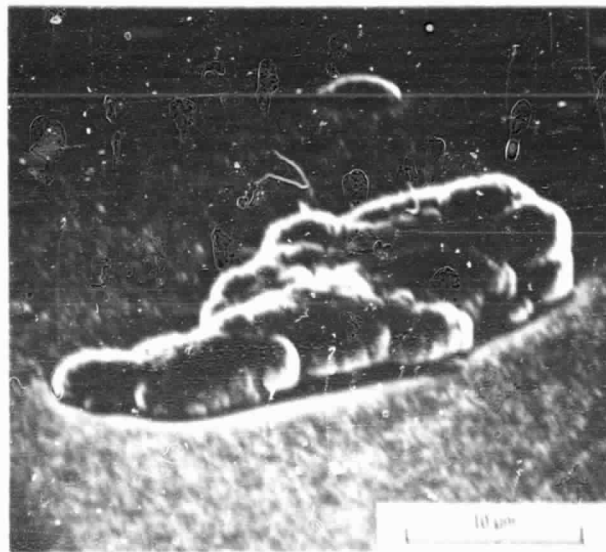
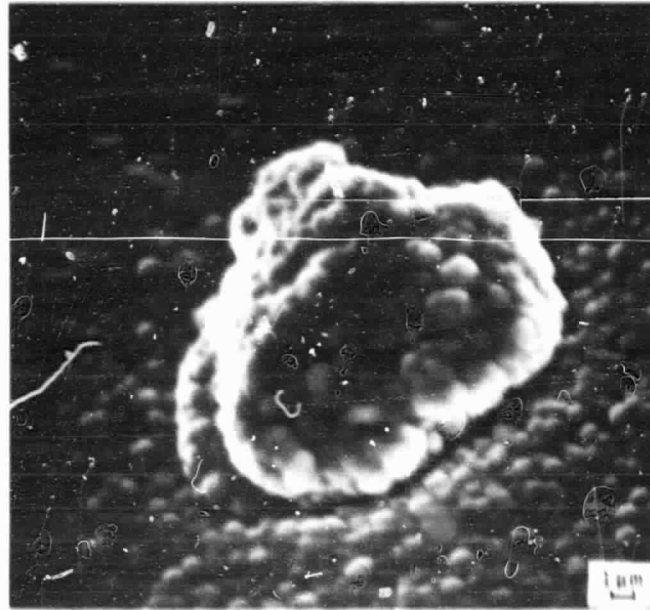


Figure 12. The variation of friction coefficient with film thickness.

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EXTREME LOCALIZED OUTGROWTH

Figure 13. Surface view of sputtered Al_2Si_2 and Cr_3C_2 film.